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The thermal crystallization behavior of cross-linked rubbers formed by endlinking monodisperse and bidisperse linear polytetrahydrofurans was investigated. The introduction of crosslinkages in PTHF inhibits the ability of chain units in proximity to the crosslinks to crystallize. From melting point depression measurements, it is estimated that the suppression in crystallizability extends as much as 15 chain units away from the crosslinkage. This estimate is consistent with the degree of equilibrium crystallinity measured in the various PTHF networks. The equilibrium melting point for uncrosslinked PTHF was deduced from melting point depression in the crosslinked rubbers to be 368° K. This is in satisfactory agreement with the  $T_m^0$  determined for linear PTHF, 361° K, but significantly higher than previously reported values. The distribution in the lengths of network chains exerted a trivial influence on thermal crystallization behavior, at least under the present experimental conditions.

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Thermal Crystallization of Polytetrahydrofuran Networks

by

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Thermal Crystallization of Polytetrahydrofuran Networks

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## INTRODUCTION:

Polytetrahydrofuran (poly[tetramethyleneoxide]) is often employed as the soft segment in polyurethane and polyester block copolymers, although the homopolymer itself has negligible commercial utility. PTHF rubbers can serve as useful model systems for the study the mechanical and crystallization behavior. The present study was undertaken to characterize the influence of crosslinking on the thermal crystallinity of polytetrahydrofuran. Both unimodal and bimodal networks, formed from end-linking of linear PTHF, were studied using differential scanning calorimetry. The thermodynamic stability of the crystalline state, as reflected in the equilibrium melting temperature,  $T_m^0$ , was determined for the different PTHF rubbers. Equilibrium melting refers to the melting of crystals devoid of interfacial effects and internal defects. Approaches for determining  $T_m^0$  include the use of low molecular weight analogues [1] or "infinitely" slow heating rates [2], as well as the extrapolation of the melting temperatures obtained at increasing annealing times [3], or increasingly high crystallization temperatures [4-6]. This latter method was employed herein to determine the effect of network structure on the equilibrium melting of PTHF rubbers. In a cross-linked material the network junctions are inherent defects, expected to inhibit both the extent and the stability of the crystalline phase. The influence of the length of network chains and dispersity of this length on the crystallization behavior of PTHF was examined.

## EXPERIMENTAL:

The polytetrahydrofuran rubbers were prepared and characterized by Prof. R.S. Stein and Dr. L. Jong of the University of Massachusetts. Various unimodal and bimodal networks formed from linear PTHF of various molecular weights were studied (see Table I). An allyl terminated linear polymer, of molecular weight between 990 to 8550, was crosslinked with a stoichiometric amount of pentaerythritol tetrakis (3-mercaptopropionate) to form the unimodal network [7]. Bimodal network were prepared by random endlinking linear polymers of molecular weight equal to 8290 and 990 respectively in the proportions cited in Table I. In this report, the samples are referred to by the molecular weight between crosslinks ( $M_c$ ), with designations for the unimodal networks prefaced by a "U", the bimodal by a "B", and the linear prepolymers by an "L". To the extent that the end-linking reaction is perfectly executed, the polydispersity of the network is of course equivalent to that of the linear precursor polymer. As determined from GPC, the polydispersity of the latter were in all cases less than 1.3 [7].

The melting behavior of the materials was characterized using differential scanning calorimetry (DSC). Most of the data were obtained on a Perkin Elmer DSC 2 with liquid nitrogen cooling. Some experiments were conducted on Perkin-Elmer DSC 7 instruments with either an intercooler or ice water cooling. Calibrations were performed daily using the two transitions of

cyclohexane for the lower temperature calorimeter, and with indium for the DSC 7 instruments. The consistency within a given day (i.e., while the calorimeter head was maintained at low temperature) was 0.1 degree standard deviation.

Samples were enclosed in sealed aluminum pans and weighed less than 10 mg. Scanning rates were 10 degrees per minute unless otherwise noted. Prior to quenching to a temperature for crystallization, the samples were annealed five minutes at 338° K, above which the stability of the PTHF is uncertain [7]. Experiments utilizing higher melting temperatures gave no indication of any memory effects (e.g., residual nucleation). Quenching from 338° K to the lowest temperature utilized (163° K) required several seconds, as indicated by the ability of the calorimeter to control the furnace temperature.

## RESULTS:

### (Equilibrium Melting Temperatures)

The PTHF rubbers were crystallized at a series of temperatures and the resulting melting points obtained from DSC. An extrapolation of the experimental  $T_m$  versus the temperature of crystallization,  $T_c$ , to the value  $T_m = T_c$  is an established method for determination of the equilibrium melting temperature [4-6]. A linear relationship between  $T_m$  and  $T_c$  is expected provided the fold length of the crystal is constant and much less than the other crystallite dimensions, and assuming no recrystallization occurs during the DSC measurement [4]. Each sample herein was allowed to develop on the order of 2-10 J/g crystallinity at the chosen  $T_c$ . A low level of crystallinity is utilized in order to minimize any isothermal thickening due to an increase in the crystal fold length. Data could be obtained over a 10 to 15 degree range of  $T_c$ 's, beyond which the crystallization was either inconveniently slow or too fast to be executed isothermally.

Figure 1 depicts Hoffman-Weeks plots for the various PTHF rubbers. In the spirit of the Hoffman-Weeks analysis, wherein consideration is focussed on the most stable crystals, the melting temperature was taken to be that at which the endotherm returns to the baseline. Extrapolation of the  $T_m$  versus  $T_c$  data in Figure 1 to the  $T_m = T_c$  value yields the equilibrium melting point,  $T_m^0$ , for each material. The results of linear least squares fitting of the higher  $T_c$  data are displayed in Figure 2 and Table II. For both unimodal and bimodal networks, the equilibrium melting point increases with  $M_c$ . The spread between the values for the two network types is probably not experimental scatter, but reflects actual effects of the network structure. The melting point depression is not a unique function of  $M_c$ ; evidently the distribution of chain lengths between crosslinks influences the melting behavior. The stability of the crystal phase has a more complex dependence on chain length and its distribution than can be captured by a simple average length between crosslinks as

represented by  $M_c$ . The lower  $M_c$  bimodal networks have higher equilibrium melting temperatures than unimodal networks of similar  $M_c$ ; this likely reflects the presence of long sequences ( $M_c = 8290$ ) of PTHF in the former. At average strand lengths exceeding 5000, however, the unimodal network, lacking the short ( $M_c = 990$ ) sequences, forms a more stable crystalline phase.

Crosslinking reduces both the extent and stability of the crystalline phase [8]. The crosslink junctions *per se* can not crystallize; moreover, they constrain topologically neighboring chain units from incorporation into the crystal phase. If consideration is given only to the non-crystallizability of the crosslinks, the melting point depression is given by [8]

$$1/T_m - 1/T_m^\infty = R/H^e f \quad \{1\}$$

in which  $H^e$  represents the (excess) enthalpy of fusion,  $R$  the gas constant, and  $T_m^\infty$  the melting point of infinitely long chains. The fraction of chain units that are crosslinked is given by

$$f = m/2M_c \quad \{2\}$$

where  $m$  is the monomer molecular weight. The correspondence of equation 1 to expressions for the melting point of copolymers is obvious [9]. The limited validity of this analogy becomes obvious in noting the failure of previous attempts to use equation 1 to account for melting point depressions observed in crosslinked cis-1,4-polybutadiene [10], polyethylene [11], and cis-1,4-polyisoprene [12]. The effect of crosslink density on the  $T_m^\circ$  of PTHF is likewise much greater than predicted by equation 1.

Crosslinking has been found to effect a reduction in the size and perfection of subsequently formed crystallites [8,11,12]. This will result in a suppression of the crystal phase stability, and thus  $T_m$ , beyond that due to the truncation of crystallizable sequence lengths accounted for in equation 1. If it is assumed that the only influence of crosslinking is to restrict a portion of the network chain, beyond just the crosslink junction itself, from incorporation in the crystal, a measure of the extent to which chain units are precluded from crystallization can be obtained by application of equation 1. The fraction of chain units unable to crosslink due to their proximity to a network junction,  $f_{eff}$ , is taken to be an adjustable parameter for fitting equation 1 to the experimental results. This approach requires values for  $H^e$  and  $T_m^\infty$ . A value of 14.5 kJ/mole was used for the perfect heat of fusion of PTHF [13]; this is 2.5 kJ/mole larger than an earlier determination [14]. A reliable assessment of  $T_m^\circ$ , however, is lacking.

The equilibrium melting temperature of sample L8551 was determined to equal 361° K, which is significantly larger than

a value reported for hydroxy terminated linear PTHF, for which  $T_m^\circ = 321^\circ \text{ K}$  for a molecular weight equal to 6760 [15]. Results published for linear PTHF of other molecular weights [15-17] are collected in Table III; surprisingly all these previous values are lower than the values determined herein for U5880 and U8551. It is difficult to reconcile higher equilibrium melting points for the crosslinked polymers. In addition to their shorter sequence length of crystallizable units, upon crystallization network chains can induce lower entropy configurations in the amorphous phase. These effects hinder crystallization, promoting smaller, less perfect crystals [8,11,12], and thus the expectation of lower  $T_m^\circ$ . Since the melting point reflects the stability of the crystalline phase relative to that of the melt, the higher melting points obtained for networks herein compared to published data for linear PTHF may reflect the influence of the chemical modification of those chain units which become network junctions. The lower  $T_m^\circ$  previously found for hydroxy terminated PTHF [15-17], compared to the present results for either linear or crosslinked PTHF containing pentaerythritol tetrakis(3-mercaptopropionate) or its reaction product with allyl endgroups, may suggest a significantly lower chemical potential for the amorphous phase of the former.

Equation 1 was fitted to the equilibrium melting point data measured for various crosslink densities by adjustment of both  $T_m^\infty$  and  $f_{\text{eff}}$ . The calculated curve agrees satisfactorily with the experimental data (Figure 2), recognizing the neglect of network modality in fitting of the data. The obtained best fit  $T_m^\infty$ , representing the melting temperature of perfect crystals formed from infinitely long, linear chains, equaled  $368^\circ \text{ K}$ . This is consistent with the  $T_m^\circ (= 361^\circ \text{ K})$  determined for linear PTHF. The ratio of the best fit value for the fraction of non-crystallizable units to the actual fraction of crosslinked units (i.e.,  $f_{\text{eff}}/f$ ) provides a measure of the number of chain units restrained from crystallizing by a crosslink junction. The calculated curve in Figure 2 corresponds to roughly 60 non-crystallizable monomer units per crosslink, which would suggest that a junction constrains on the average as many as 15 adjoining units from incorporation into the crystal phase. This is probably an overestimate, since some of the reduction in  $T_m^\circ$  upon crosslinking arises from reduced perfection of the crystallites [8,11,12], an effect unaccounted for by equation 1. While  $f_{\text{eff}}$  was deduced herein from melting point suppression, it is of interest to compare this value with the actually measured crystallinity of the crosslinked PTHF.

*(Ultimate crystallinity)*

A comparison was made of the extent of crystallization after annealing at  $233^\circ \text{ K}$ . The crystallization was continued until the degree of crystallinity became invariant. For

networks of lower crosslink density essentially complete crystallization was achieved in less than an hour, whereas, for example, PTHF with  $M_c = 2000$  required about two hours at  $233^\circ\text{K}$  for equilibrium to be attained. The results are displayed in Figure 3 and Table II (wherein a small correction to the measured melting enthalpies has been made to adjust for the weight of the endlinker). Of course the more crosslinked PTHF crystallizes less. From the fraction of non-crystallizing chain units deduced from the melting point depression for each network, a prediction of the dependence of the degree of crystallinity on  $M_c$  can be made. It is assumed that the degree of crystallinity of crosslinked PTHF is proportional to that of L8551, with the proportionality constant equal to  $f_{\text{eff}}/1+f_{\text{eff}}$ . As seen in Figure 3, the agreement between the extent of crystallization predicted in this manner and the experimentally measured crystallinities is acceptable. The implicit assumption herein of equivalent perfection in the crystalline phase of the various networks is probably not valid. Crosslinking reduces both the size and perfection of crystallites, and both influence the apparent degree of crystallinity as inferred from the measured heats of fusion. Nevertheless, the data in Figure 3 indicates that the  $f_{\text{eff}}$  deduced from melting points is consistent with the actual levels of crystallization in the crosslinked PTHF.

*(Long-term crystallinity)*

After prolonged storage ( $> 6$  months) at room temperature (circa  $296^\circ\text{K}$ ) no crystallization of the highly crosslinked networks (i.e., U2000, B2000, and U2520) was observed, while PTHF rubbers with lower crosslink densities exhibit multiple melting peaks. To more fully characterize the long time crystallization behavior, samples of U5880 and U8551 were melted at  $338^\circ\text{K}$  for 5 minutes, annealed for varying time periods at room temperature, and then analyzed calorimetrically. For both samples after one day annealing, two melting endotherms appear, at about  $304^\circ\text{K}$  and  $312^\circ\text{K}$  respectively. The melting temperatures of the U8551 are slightly higher than those of the U5880 through about 12 days of crystallization, after which the  $T_m$  are essentially equivalent. The location of the higher temperature peak appears to be independent of crystallization time, while the temperature of the lower peak increases during crystallization, eventually merging with the higher temperature transition. Whether the lower temperature endotherm can be associated with hindered inter-lamellar spherulitic growth [17,18] is speculative. The disappearance of the lower melting peaks after sufficient annealing at these high (relative to  $T_m$ ) temperatures may reflect rearrangement of such inter-lamellar crystallites. Over the course of the present experiment (37 days), the enthalpy of melting of the U5880 never exceeded 3 J/g.



In an attempt to assess the influence of crystal thickening on the melting behavior, the shape of the long term melting endotherm was studied as a function of heating rate. With slow heating, metastable crystals conceivably have time to reorganize to a more stable form; thus, the intensity of their melting endotherm may decrease relative to that of the more stable form [19-21]. Network U5880 (Figure 4) shows two melting endotherms, regardless of the rate of heating. However, the effect of changes in heating rate provide no indication of reorganization of metastable crystals to a more stable form. It is seen in Figure 4 that at sufficiently slow heating rates, U8551 exhibits three melting endotherms. At higher rates of heating the lowest melting peak disappears, suggesting that it may represent crystalline entities formed during the course of the calorimetry.

The intermediate peak in the U8551 data of Figure 5 responds to changes in heating rate in a manner consistent with a metastable crystalline form. It exhibits a melting point increase with both higher heating rate and prolonged annealing at 296° K. Coincident with this increase in  $T_m$  during annealing, there occurs a substantial increase in the extent of crystallinity for the U8551 after 15 days. The heat of fusion increases from 2.5 J/g to 45 J/g over 2 days time. An induction period followed by rapid crystallization suggests a homogeneous crystallization process. The glass transition temperature of linear PTHF is 111 degrees below room temperature [14,22]; accordingly, at room temperature minimal kinetic hindrance of crystallization is expected. Nucleation of crystallization will be suppressed, however, by proximity to the melting point. The behavior of U8551 in Figure 5 reflects slow nucleation, followed by rapid growth of the crystalline phase. The sharp reduction in the growth after roughly 15 days is probably associated with the development of impingement between neighboring spherulites, as has been directly observed in linear PTHF [17,18].

#### SUMMARY

The introduction of crosslinkages in PTHF inhibits the ability of chain units in proximity to the crosslinks to crystallize. From melting point depression measurements, it is estimated that the suppression in crystallizability extends as much as 15 chain units away from the crosslinkage. This estimate is consistent with the degree of crystallinity measured in the various PTHF networks.

The equilibrium melting point for uncrosslinked PTHF was deduced from melting point depression in the crosslinked rubbers to be 368° K. This is in satisfactory agreement with the  $T_m^\circ$  determined for linear PTHF, 361° K, but significantly higher than previously reported values. The distribution in the lengths of network chains exerted a trivial influence on thermal crystallization behavior, at least under the present experimental conditions. This is in marked contrast to

expectations for orientational crystallization.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

1. P.J. Flory and A. Vrij, J. Amer. Chem. Soc. 85, 3548 (1963).
2. A. Quinn and L. Mandelkern, J. Amer. Chem. Soc. 80, 3178 (1958).
3. K. Kamide, K. Ohno, T. Kawai, Die Makromol. Chemie 137, 1 (1970).
4. J.D. Hoffman, J. J. Weeks, J. Res. Natl. Bur. Stand. 66A, 13 (1962).
5. M. Magalan and L. Mandelkern, J. Phys. Chem. 71 3833 (1967).
6. B. Wunderlich, Macromolecular Physics, Vol. 3, Academic Press, New York, 1980, page 33.
7. R.S. Stein and L. Jong, private communication.
8. L. Mandelkern, Crystallization of Polymers, McGraw Hill, New York, 1964, Chapter 6.
9. P.J. Flory, Principles of Polymer Chemistry, Cornell Univ., Ithaca, 1953, page 570.
10. W. Fahn and J. Majer, Angew. Chem. 68, 345 (1956).
11. L. Mandelkern, D.E. Roberts, J.C. Halpin, and F.P. Price, J. Am. Chem. Soc. 82, 46 (1960).
12. D.E. Roberts and L. Mandelkern, J. Am. Chem. Soc. 82, 1091 (1960).
13. I.J.W. Bowman, D.S. Brown, and R.E. Wetton, 10, 715 (1969).
14. S. Machida, H. Suga, and S. Seki, Polymer J. 5, 25 (1973).
15. G.S. Trick, J. M. Ryan, J. Poly. Sci. C 18, 93 (1967).

16. A.G. Margaritis and N.K. Kalfogiou J. Poly. Sci. Poly. Phys. Ed. 27, 1767 (1989).
17. F.P. Warner, D.S. Brown and R.E. Wetton, J. Chem. Soc. Faraday Trans. I 72, 1064 (1976).
18. F.P. Warner, D.S. Brown and R.E. Wetton, Polymer 22, 1349 (1981).
19. S.X.D. Cheng, B. Wunderlich, J. Poly. Sci. Poly. Phys. Ed. 26, 1947 (1988).
20. S.X.D. Cheng, D.W. Noid and B. Wunderlich, J. Poly. Sci. Poly. Phys. Ed. 27, 1149 (1989).
21. C.P. Buckley and A.J. Kovacs in Structure of Crystalline Polymers (J.H. Hall, ed.) Elsevier, New York, 1984, page 261.
22. P. Dreyfuss in Handbook of Elastomers - New Developments and Technology (A.K. Bhowmick and H.L. Stephens, ed.) Marcel Dekker, New York, page 695.

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 Table I. Composition of Materials  
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<u>Sample</u>	<u>Mole Fraction:</u>						<u>Endlinker</u>
	<u>992</u>	<u>2000</u>	<u>2520</u>	<u>5880</u>	<u>8286</u>	<u>85</u>	
U2000	--	0.67	--	--	--	--	0.33
U2520	--	--	0.67	--	--	--	0.33
U5880	--	--	--	0.67	--	--	0.33
U8286	--	--	--	--	0.67	--	0.33
U8551	--	--	--	--	--	0.67	0.33
B2000	0.58	--	--	0.09	--	--	0.33
B2520	0.53	--	--	0.14	--	--	0.33
B5880	0.22	--	--	0.45	--	--	0.33

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Table II. Thermal Crystallization Results

Network	$T_m^\circ$ (K) <sup>1</sup>	$H_f$ (J/g)	
		measured <sup>2</sup>	calculated <sup>3</sup>
U2000	267	37.0	40.
U2520	305	44.3	45.
U5880	344	53.9	61.
U8286	349	56.1	66.
U8551	---	56.5	67.
B2000	307	32.0	40.
B2520	309	37.6	45.
B5880	329	55.9	61.
L8551	361	83.9	---
L10160	---	82.8	---

<sup>1</sup> from Hoffman-Weeks extrapolation.

<sup>2</sup> equilibrium degree of crystallization at -40° C.

<sup>3</sup> based on the suppression of crystallinity deduced from  $T_m^\circ$  (using equation 1 and the best-fit  $f_{eff}$ ).

Table III - Equilibrium Melting Points for Linear PTHF

<u>Molecular Weight</u>	<u>T<sub>m</sub><sup>o</sup> (K)</u>	<u>Method</u>	<u>Reference</u>
3,000	327	Hoffman-Weeks	16
6,760	320	Hoffman-Weeks	15
8,551	361	Hoffman-Weeks	this work
130,000	324	Hoffman-Weeks	15
230,000	343	asserted	17

### Figure Captions

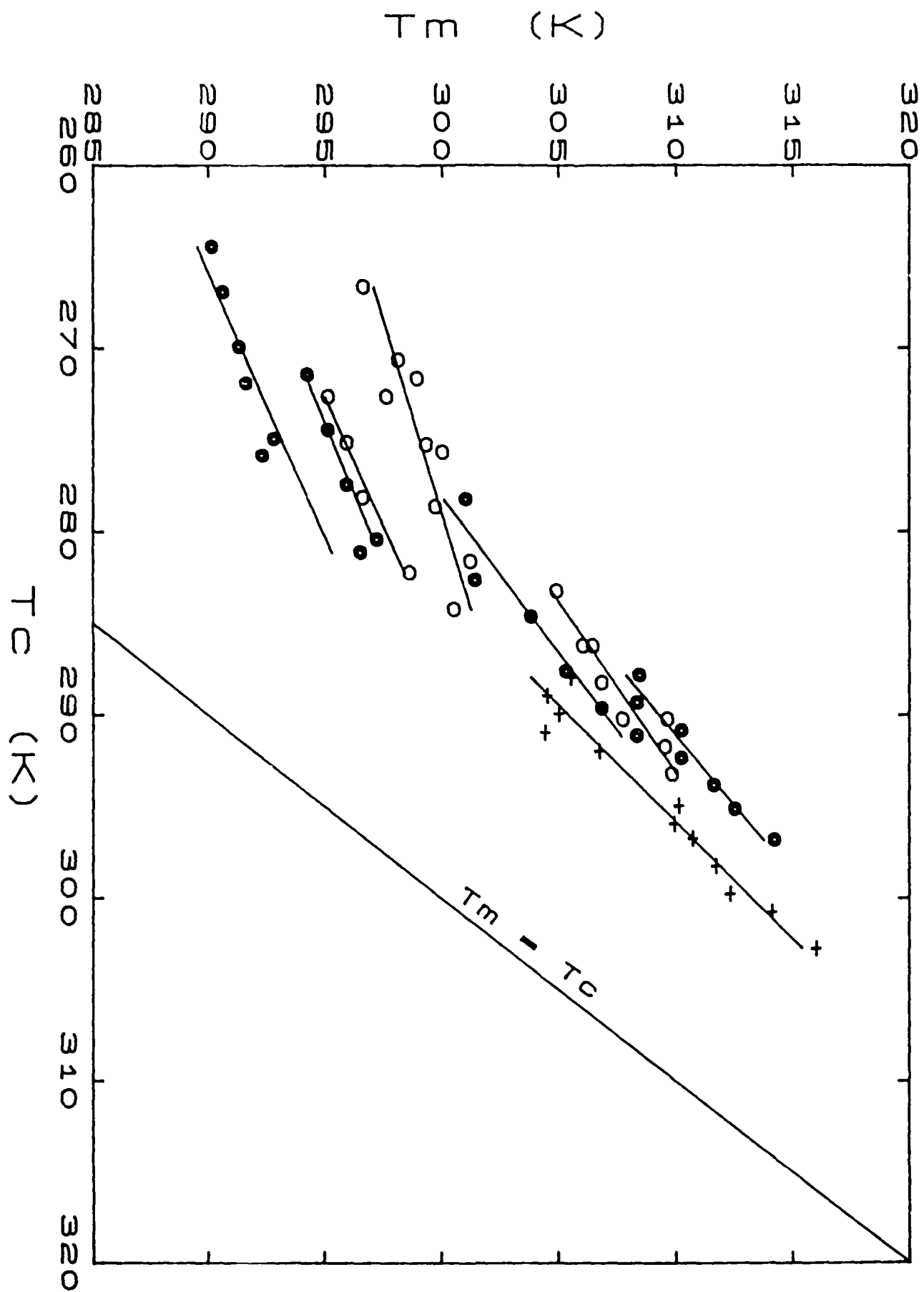
Figure 1 - The melting points measured for the PTHF rubbers at various crystallization temperatures. The filled and open circles represent data for the unimodal and bimodal networks respectively, while the crossed refer to L8551. The equilibrium melting temperatures determined by linear extrapolation to the intersection with the  $T_m = T_c$  line are given in Table II.

Figure 2 - The equilibrium melting temperatures for PTHF rubbers of various crosslink density determined from the data in Figure 1. There is no obvious effect of network architecture (unimodal and bimodal represented by filled and open circles respectively). The solid line denotes the dependence of  $T_m^\circ$  on  $M_c$  calculated from equation 1 using best-fit values of  $T_m^\infty = 368^\circ \text{ K}$  (cf.  $T_m^\circ = 361^\circ \text{ K}$  for L8551) and  $f_{\text{eff}} = 60f$ .

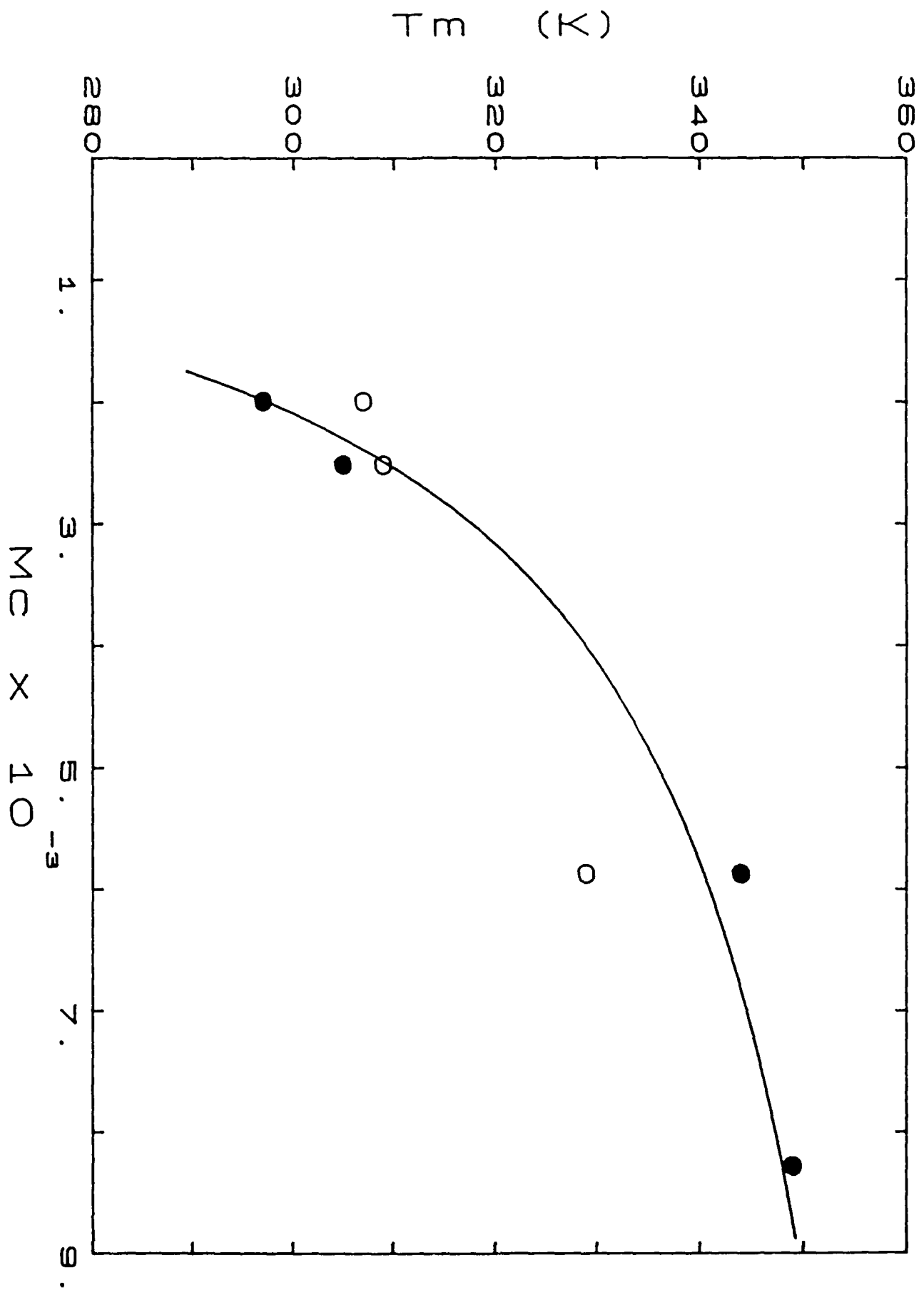
Figure 3 - The dependence on crosslink density of the equilibrium degree of crystallinity for  $-40^\circ \text{ C}$ , using  $201 \text{ J/g}$  as the perfect heat of fusion [13]. The symbols are as defined in Figure 2. The curve represents the crystallinity predicted from the measured melting point depressions.

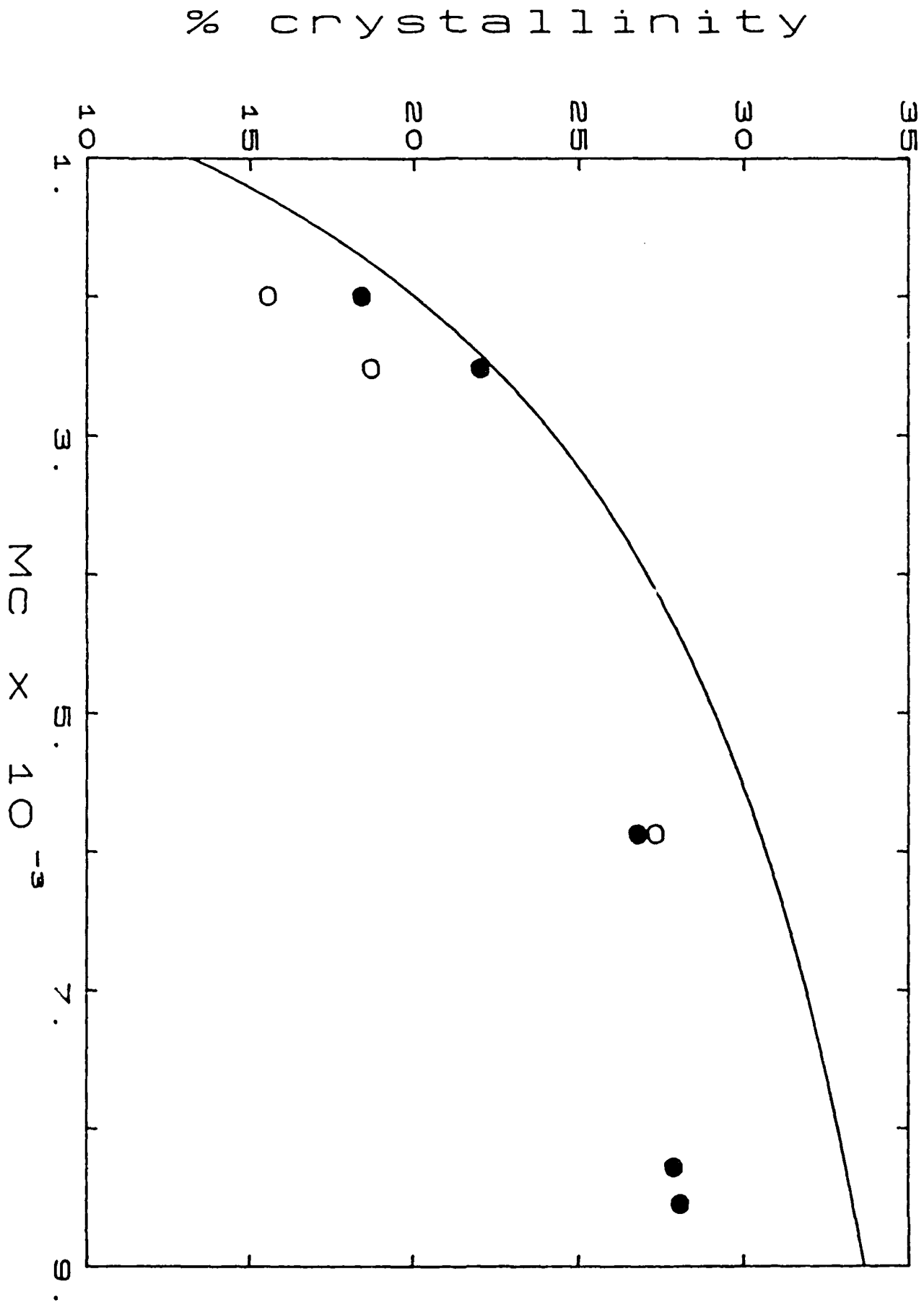
Figure 4 - Calorimetry results for U5881 at the indicated heating rates (in degrees per minute).

Figure 5 - Calorimetry results for U8551 at the indicated heating rates (in degrees per minute).









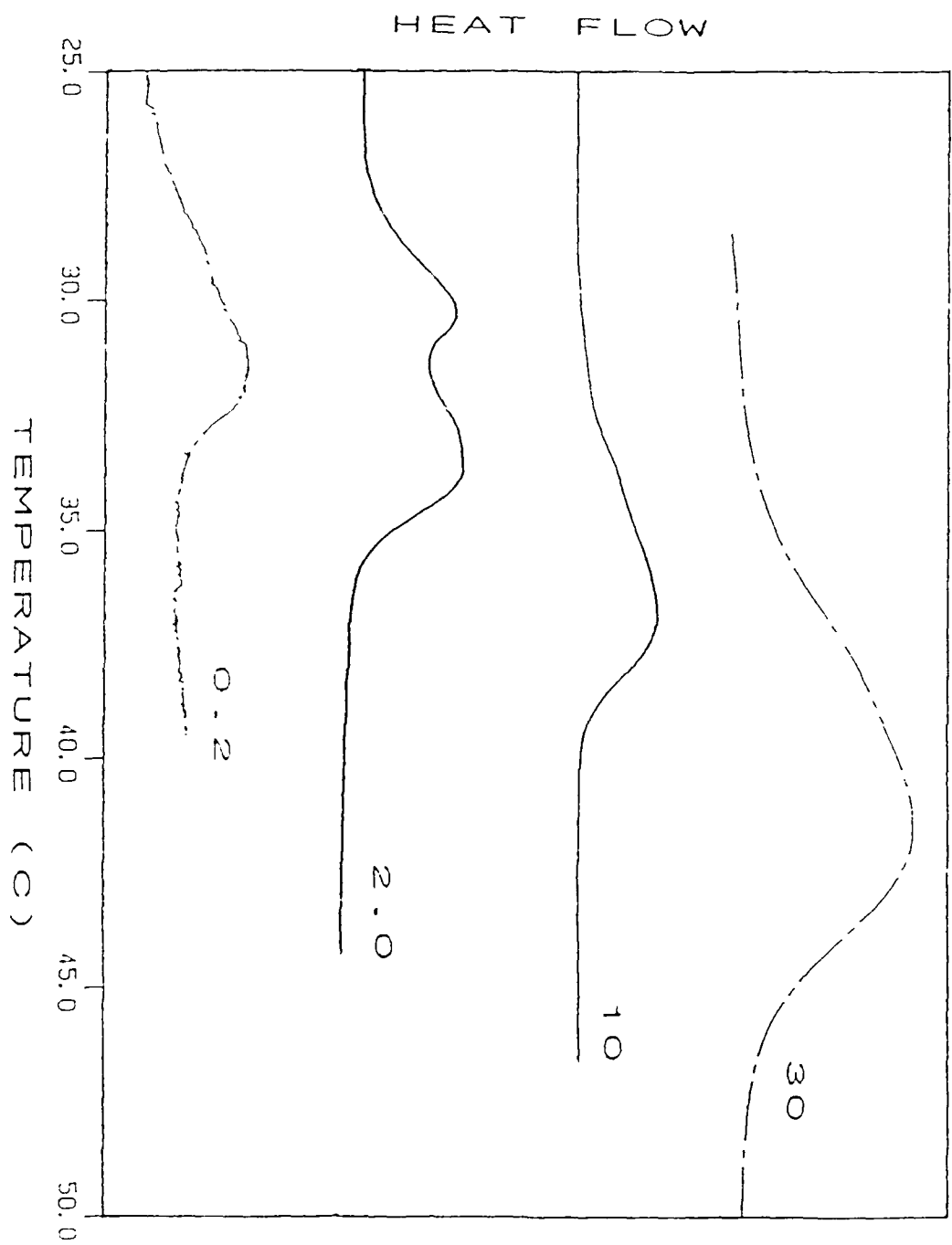
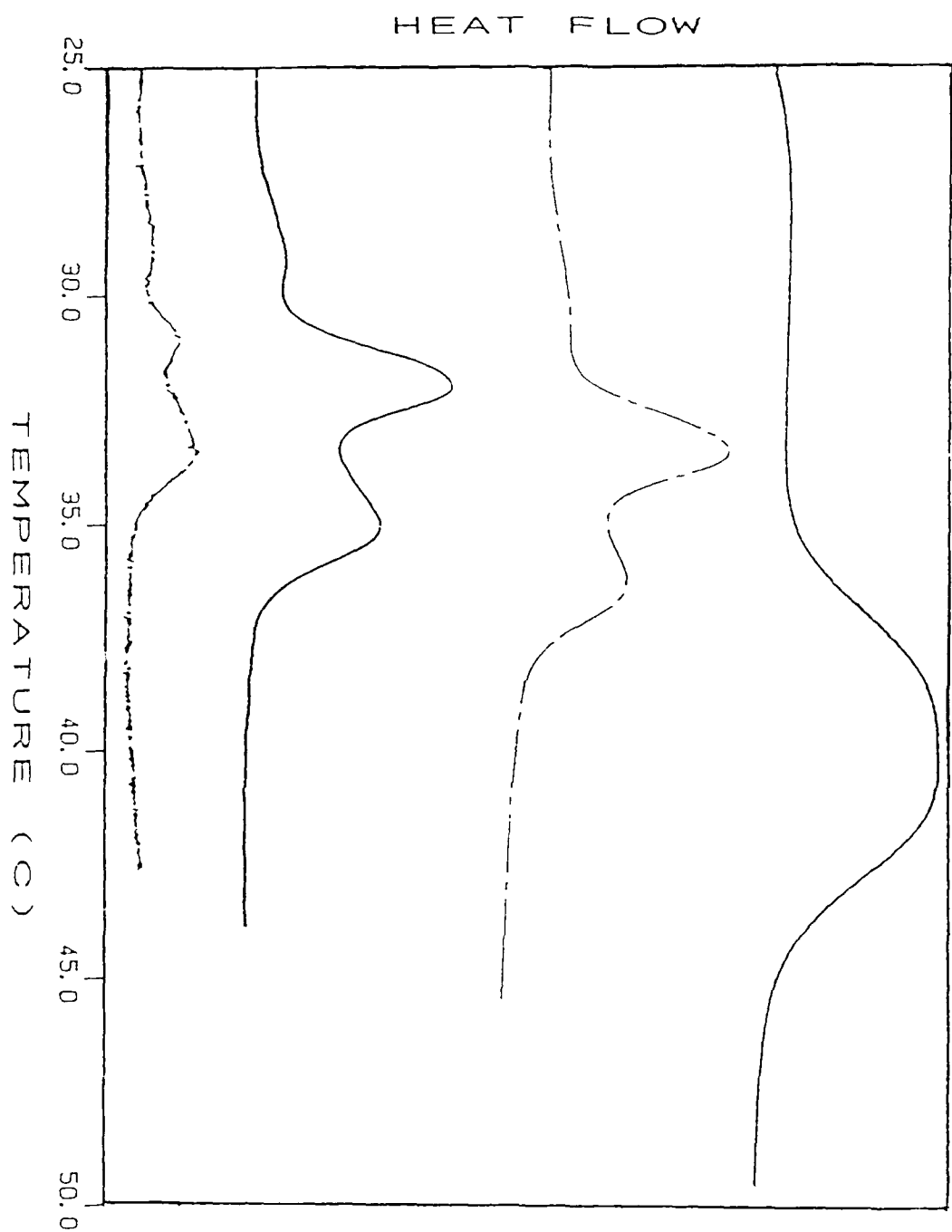


FIG 4



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